

BIRLA INSTITUTE OF TECHNOLOGY, MESRA, RANCHI
(END SEMESTER EXAMINATION)

CLASS: IMSC, MSC
BRANCH: CHEMISTRY

SEMESTER : IX/I
SESSION : MO/2022

SUBJECT: CH405 & CH405R1 PRINCIPLE OF ORGANIC SYNTHESIS

TIME: 3:00 Hours

FULL MARKS: 50

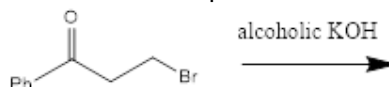
INSTRUCTIONS:

1. The question paper contains 5 questions each of 10 marks and total 50 marks.
2. Attempt all questions.
3. The missing data, if any, may be assumed suitably.
4. Before attempting the question paper, be sure that you have got the correct question paper.
5. Tables/Data hand book/Graph paper etc. to be supplied to the candidates in the examination hall.

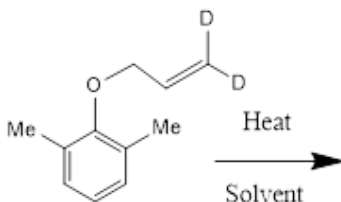
Q.1 Explain the following (any five questions) (2x5=10)

- (i) Conformational free energy values of Cl and I atoms in cyclohexane systems are almost identical, even though the size of iodine is larger than that of chlorine.
- (ii) *Trans*-2-chlorocyclohexanol gives epoxy cyclohexane under basic conditions whereas *cis*-isomer gives cyclohexanone under the same conditions,
- (iii) *Trans*-4-*t*-butylcyclohexane carboxylic acid is a stronger acid than its *cis*- isomer.
- (iv) Ethyl *trans*-4-*t*-butyl cyclohexane carboxylate undergoes base catalysed hydrolysis faster than its *cis*- isomer.
- (v) *Cis*-4-*t*-butylcyclohexanol undergoes faster oxidation with chromic acid than its *trans*-isomer.
- (vi) Both *cis*- and *trans* -1,2-dibromo cyclohexane, on treatment with I⁻ (iodine minus) give cyclohexene.

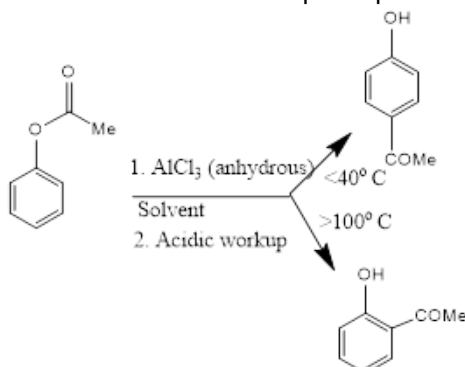
Q.2(a) There can be two possible mechanisms (E1 and E1CBrev) for the β-elimination of the following 3
bromide which does not show any primary kinetic isotope effect (k_H/k_D = 1). Write the mechanisms. How can you tell which method is operative?



Q.2(b) Write the product in the following pericyclic reaction along with its mechanism of formation. 2
Give one chemical proof in support of the mechanism.



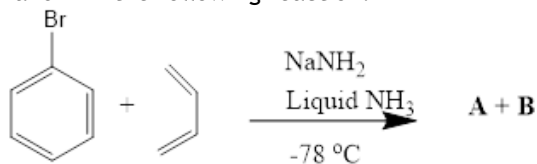
Q.2(c) Consider the following reaction and answer the subsequent questions: 3



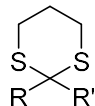
- i) Write the mechanism of the reaction for anyone of the product.
- ii) Which one is kinetically controlled, and which one is the thermodynamically product?
- iii) Explain why the ortho isomer is obtained as a major product at higher temperature.

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Q.2(d) Write the structures of A and B in the following reaction: 2



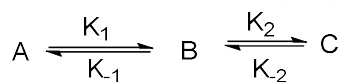
Q.3(a) 1,3-Dithiane is not deprotected to the corresponding carbonyl compound with acid, but in the presence of HgCl_2 it is cleaved accordingly. Explain 2



Q.3(b) Explain why alkynes are less reactive than alkenes towards addition of bromine. 2

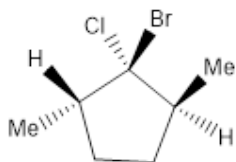
Q.3(c) How will you prove whether a reaction is intramolecular or intermolecular? Explain with examples. 2

Q.3(d) Draw a reaction coordinate diagram for the following reaction which 'C' is the most stable and 'B' is the least stable of the three species, and the transition going from 'B' to 'C'. 1x4=4

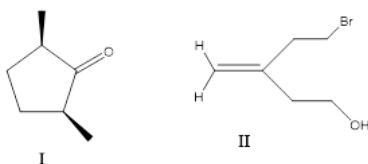


- (i) How many transition states are there?
- (ii) Which is faster step in forward reaction?
- (iii) Which is the rate determining step in the forward direction?

Q.4(a) (i) Identify the stereochemical relation (Topicity) of the two methyls in the following molecule: 2+1+1=4
Explain your answer.

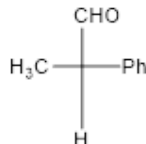


(ii) Assign the Re/Si descriptor for the α -face around the sp^2 -carbon in each of the following molecules:

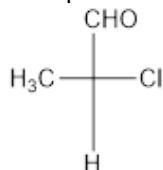


(iii) Which one of the chlorines Cl_a or Cl_b is pro-R in the following molecule? Show how you have arrived at the answer.

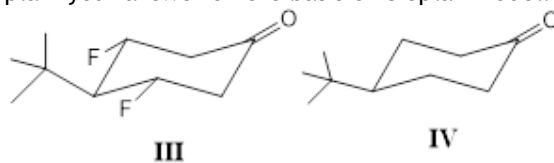
Q.4(b) As per Cram's open chain model, draw the favoured reacting conformation in which the following aldehyde reacts with NaBH_4 and then draw the predominant product after work up. 2



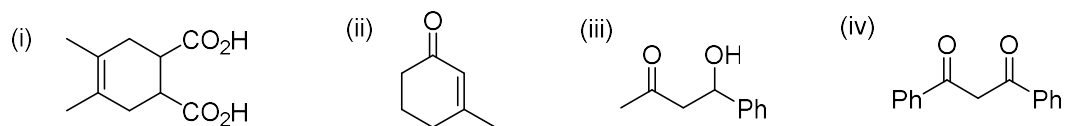
Q.4(c) As per Felkin-Anh model, draw the favoured reacting conformation in which the following aldehyde reacts with CH_3Li and then draw the predominant product after workup. 2



Q.4(d) Which one of the following ketones will give a greater percentage of equatorial alcohol when reduced with NaBH_4 ? Explain your answer on the basis of Cieplak model. 2



Q.5(a) Give retrosynthetic analysis and an efficient synthesis of each of the following compounds 2x4=8 (answer any two questions)



Q.5(b) Explain with proper examples the meaning of the terms “Synthetic equivalent” or “Functional group interconversion”. 2

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